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Journal

Atmospheric Environment, 44(1)

ISSN

1352-2310

Authors

Hsu, YK
VanCuren, T
Park, S
[et al.](#)

Publication Date

2010

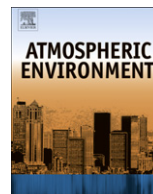
DOI

10.1016/j.atmosenv.2009.10.002

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Peer reviewed



Methane emissions inventory verification in southern California

Ying-Kuang Hsu^{a,*}, Tony VanCuren^a, Seong Park^a, Chris Jakober^a, Jorn Herner^a,
Michael FitzGibbon^a, Donald R. Blake^b, David D. Parrish^c

^a California Air Resources Board, 1001 "I" Street, Sacramento, CA 95812, USA

^b Department of Chemistry, University of California at Irvine, 570 Rowland Hall, Irvine, CA 92697, USA

^c National Oceanic and Atmospheric Administration, Chemical Sciences Division, 325 Broadway R/CSD7, Boulder, CO 80305, USA

ARTICLE INFO

Article history:

Received 1 June 2009

Received in revised form

29 September 2009

Accepted 3 October 2009

Keywords:

Methane emissions

Greenhouse gas

Emission inventory

Inventory verification

Scaling ratio method

ABSTRACT

Methane (CH₄) and carbon monoxide (CO) mixing ratios were measured at an air quality monitoring station near the Mt. Wilson (MW) Observatory in southern California starting in the spring of 2007. Diurnal variation and mixing ratio correlation ($R^2 = 0.81$) were observed. The correlation results observed agree with previous aircraft measurements collected over the greater Los Angeles (LA) metropolitan area. The consistent agreement between CH₄ and CO indicates these gases are well-mixed before reaching the sampling site and the emission source contributions of both compounds are reasonably constant. Since CH₄ and CO are considered non-reactive on the time scale of dispersion within the LA urban area and their emission sources are likely to be similarly distributed (e.g., associated with human activities) they are subject to similar scales of atmospheric transport and dilution. This behavior allows the relationship of CH₄ and CO to be applied for estimation of CH₄ emissions using well-documented CO emissions. Applying this relationship a "top-down" CH₄ inventory was calculated for LA County based on the measurements observed at MW and compared with the California Air Resources Board (CARB) "bottom-up" CH₄ emissions inventory based on the Intergovernmental Panel on Climate Change recommended methodologies. The "top-down" CH₄ emissions inventory is approximately one-third greater than CARB's "bottom-up" inventory for LA County. Considering the uncertainties in both methodologies, the different CH₄ emissions inventory approaches are in good agreement, although some under and/or uninventoried CH₄ sources may exist.

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1. Introduction

Methane (CH₄) is emitted both naturally and through human activities. It is the greenhouse gas (GHG) second only to carbon dioxide in enhanced climate forcing from the pre-industrial era (1750) to the present (Simpson et al., 2006; Hofmann et al., 2006). The global mixing ratios of CH₄ in the atmosphere have more than doubled since the pre-industrial period, rising from around 750 parts per billion (ppb) in 1800 (Simpson et al., 2002; Dlugokencky et al., 2003) to the current level of around 1770 ppb (NOAA, 2008). The rate of increase slowed to 5–10 ppb year⁻¹ by the late 1980s and continued to decline into the 1990s, though with considerable annual growth variation (Dlugokencky et al., 1994, 1998; Simpson et al., 2002). These unpredicted growth rate fluctuations have been linked primarily to non-cyclical events such as the eruption of Mt. Pinatubo in 1991, the Indonesian and boreal wildfires of 1997 and 1998, respectively, and anomalous wetland emissions in 1998 (Dlugokencky et al., 1996; Duncan et al., 2003; Prinn et al., 2005).

The California Global Warming Solutions Act of 2006 (Assembly Bill 32, AB 32, Núñez) requires the California Air Resources Board (CARB) to report and verify the statewide GHG emissions inventory (COLC, 2006). To support the AB 32 program, CARB developed a statewide GHG emissions inventory that provides estimates of the amount of GHG released to the atmosphere by human activities annually within California (CARB, 2008a). The CARB inventory was developed using the Intergovernmental Panel on Climate Change (IPCC) recommended methodologies and covers the years 1990–2004. These GHG emissions estimates rely primarily on state, regional or national data sources, rather than individual facility-specific emissions. CARB's GHG inventory uses a "bottom-up" approach and is calculated based on emission factors (e.g., grams of CH₄ per gallon of gasoline combustion) multiplied by activity data (e.g., gallons of gasoline combusted). This inventory provided the basis for developing the 1990 statewide emissions level and 2020 emissions limit required under AB 32. CARB's emission reduction program relies on accurate knowledge of the emissions to ensure that reductions are actually achieved.

In California, the main anthropogenic emission sources of CH₄ are ruminant livestock, landfills, wastewater treatment, losses

* Corresponding author. Tel.: +1 916 323 5774; fax: +1 916 323 1045.

E-mail address: yhsu@arb.ca.gov (Y.-K. Hsu).

occurring during oil and gas extraction and transmission, combustion of fossil fuels and biomass, and rice cultivation (CARB, 2008a). Natural sources of CH_4 are dominated by wetlands. The primary sink for CH_4 is its destruction in the atmosphere by hydroxyl radicals (Prinn et al., 1995, 2001). Some CH_4 is also oxidized by microorganisms (called methanotrophs), which use CH_4 as a source of carbon and energy. Tropospheric CH_4 is eventually oxidized to carbon dioxide; its atmospheric lifetime is estimated to be 8–12 years (NOAA, 2000; Cunbold et al., 2002; IPCC, 2007).

The objectives of this study were to conduct a pilot program to measure atmospheric CH_4 mixing ratios, to estimate the CH_4 emissions inventory for Los Angeles (LA) County California using the resulting field measurements, and to assess CARB's official CH_4 emissions inventory. This paper presents CH_4 and carbon monoxide (CO) mixing ratios measured at the Mt. Wilson (MW) monitoring station. A “top-down” emission inventory estimation methodology based on the correlation between CH_4 and CO observed at MW is described, and the estimated CH_4 inventory with level of uncertainty is presented. Finally, the comparison between the “top-down” inventory estimate and CARB's “bottom-up” official CH_4 inventory for LA County is presented. Sources of uncertainty in both emission estimates are also discussed in this paper.

2. Experimental methods

An air quality monitoring station adjacent to the MW Observatory ($34^\circ 13' 21''\text{N}$, $118^\circ 3' 42''\text{W}$, elevation 1735 m) was installed in April 2007 to study GHG emissions in the LA urban area. Mt. Wilson is one of the prominent peaks in the San Gabriel Mountains, in the Angeles National Forest, and located in northern LA County. The monitoring station is south-facing overlooking the LA metropolitan area from the top of the San Gabriel Fault scarp, making it an ideal site to collect comparative air samples from both the LA urban boundary layer and overlying free troposphere. The sampled air at the station is influenced by strong and rapid upslope flow of well-mixed air from the urban lowland during daylight hours (Fig. 1), with reversed subsidence flow replacing the urban air with air from the lower free troposphere (LFT) at night. This flow pattern is typical of the southern California climate and very persistent in all seasons; the upslope flow is driven by the regular sea breeze on the coastal plain pushing urban air toward the base of the scarp, lofting

it to the monitoring site. The LFT air at MW generally arrives from the northwest, flowing off the eastern Pacific Ocean. Despite the site's proximity to the 15 million inhabitants of southern California, nighttime air at MW is generally as clean or cleaner than air measured at the background station at Trinidad Head (NOAA, 2008) on the northern California coast (VanCuren, 2008). Note that LA County splits into the Mojave Desert Air Basin to the northeast and South Coast Air Basin (SoCAB) to the south (Fig. 2). As described above, the MW monitoring station samples the SoCAB portion of LA County urban area, due to its predominant south winds.

This study included continuous real-time monitoring of CH_4 and meteorological conditions and intensive hourly canister sampling for comprehensive organic gases and CO in discrete seasonal campaigns. The four intensive sampling periods were April 28th–May 6th, 2007; September 8th–16th, 2007; November 10th–18th, 2007; and February 9th–17th, 2008. Methane was measured using two techniques: 1) cavity enhanced laser absorption spectroscopy using a tunable diode laser (TDL) analyzer (Los Gatos Research Model 908-0001) with 1 s intervals, 2) analysis of hourly-integrated canister samples with an Agilent 5890 gas chromatograph (GC) using flame ionization detection (FID). The same canister samples were also analyzed for CO using an Agilent 6890 GC-FID through packed column separation followed by catalytic conversion to CH_4 . Meteorological conditions were monitored for wind speed (Met One 010C), wind direction (Met One 020C), temperature (Met One 060-1), and relative humidity (Vaisala HMP-45D). The TDL CH_4 analyzer was calibrated daily using zero air and CH_4 standard gas (3.950 parts per million, ppm) on site. Canister samples were quantified with GCs calibrated immediately before analysis. Comparison between the two different CH_4 measurement approaches reveals good agreement (linear regression slope = 1.00, $R^2 = 0.94$). The consistency between the measurements provides confidence in the results and strengthens the validity of their application in emission inventory calculations.

3. Results and discussion

3.1. Atmospheric CH_4 and CO mixing ratios

Nighttime inversion conditions followed by strong daytime mixing frequently occur at MW. These meteorological conditions

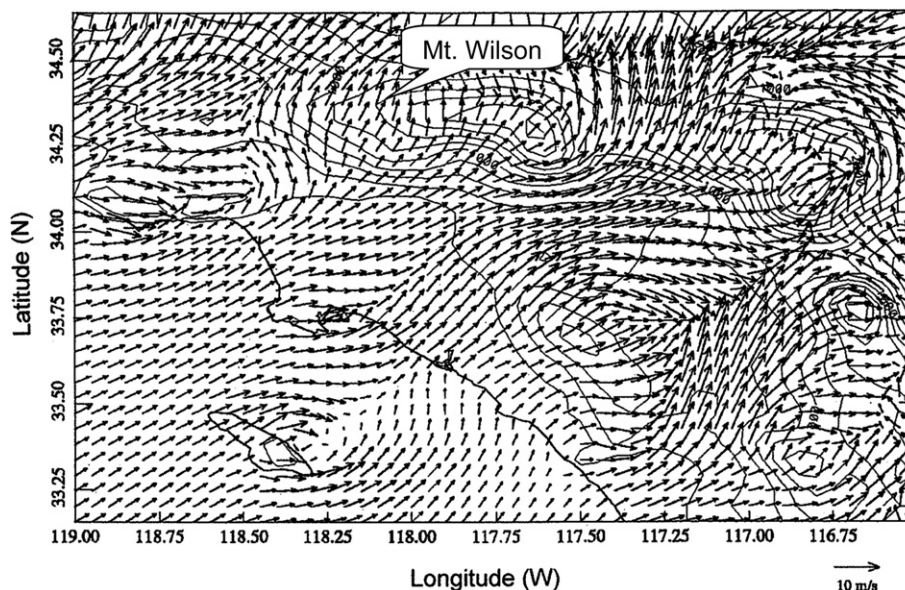


Fig. 1. Simulated surface winds in the summer afternoon (1600 PST) in the SoCAB (Stolzenbach et al., 2001 with permission).

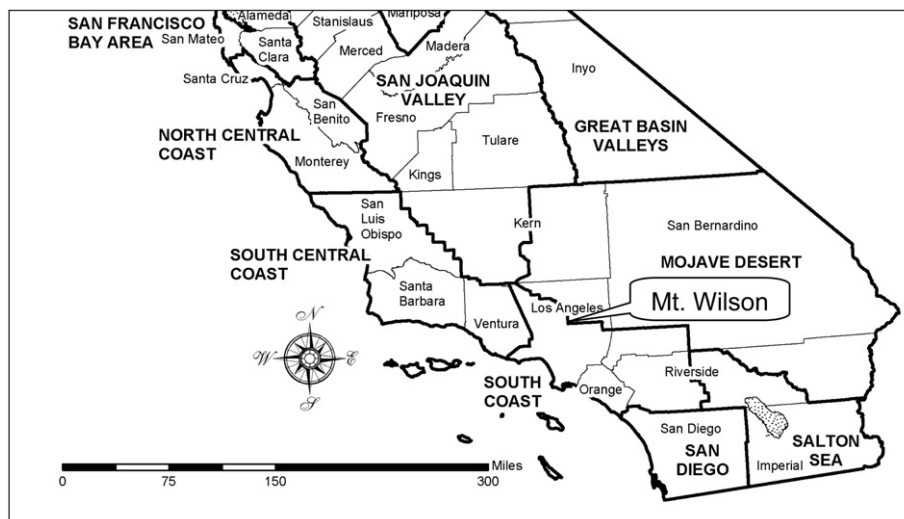


Fig. 2. California air basin (thick lines) and county (thin lines) boundaries.

lead to characteristic diurnal mixing ratio variations of CH_4 and CO emitted in LA County (Fig. 3). The quartile plots present frequency distributions of mixing ratios by hour of the day of the four intensive sampling periods, excluding mixing ratios measured on February 14, 2008 when winds were from the north. Exclusion of this date will be explained in the next section. Elevated mixing ratios of both

compounds are observed during early afternoon hours. These higher mixing ratios are attributable to influence from emission sources in LA County during midday when inversion layer heights are above the MW monitoring site and strong onshore sea breezes are pushing urban air upslope of the scarp. The observed mixing ratios ranged from 1.76 to 2.16 ppm for CH_4 and 0.055–0.725 ppm for CO, which are quite similar to the 2002 National Oceanic and Atmospheric Administration (NOAA) airborne measurements over LA (CH_4 : 1.73–2.06 ppm; CO: 0.084–0.67 ppm, Parrish, 2008). In addition, the lower CH_4 and CO levels are slightly (approximately 10 ppb) below those measured via aircraft at 2000 m above sea level near Trinidad Head, California (NOAA, 2008). The results demonstrate that the MW site observes both urban boundary layer and overlying background troposphere air masses.

3.2. Relationship between CH_4 and CO mixing ratios

The relationship between CH_4 and CO mixing ratios measured between 11 am and 6 pm at the MW monitoring station during the four discrete seasonal campaigns is presented in Fig. 4 and Table 2. Good linear correlation was observed ($R^2 = 0.81$), indicating that both gases are well-mixed before reaching the MW site and source contributions of both compounds are reasonably consistent. Even though the correlation of CH_4 and CO mixing ratios using all 24-h data gives a similar slope and correlation coefficient, we chose to use the data collected between 11 am and 6 pm for the correlation analysis as they represent both CH_4 and CO emitted from LA County and observed at the MW site (see Fig. 3). This is supported by a simulated surface wind field in the SoCAB (Fig. 1) where typical onshore and inland winds move air parcels from the western coast to the north and east of the basin from the mid-morning to late-afternoon (Stolzenbach et al., 2001). During transit from the coast, air parcels receive pollutant emissions from the sources encountered on the particular trajectory of transit. Variations of wind speed and direction about the average conditions, and intermixing of air parcels within the basin ensures that the air sampled at MW represents a wide spectrum of emission sources within the basin.

Fig. 4 includes all measurements from all four seasonal campaigns, with the exception of the data collected on February 14, 2008 when the winds were from the north. Methane and CO mixing ratios measured on this day were not impacted by emissions from the LA urban area and do not show elevated mixing ratios during early afternoon hours (Fig. 5).

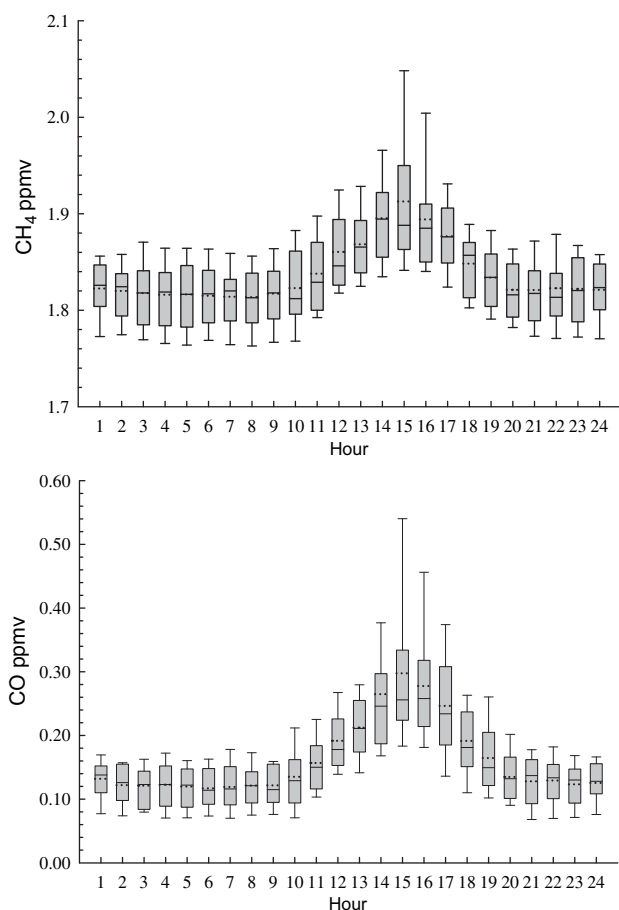


Fig. 3. Quartile plots of CH_4 and CO mixing ratios measured at the Mt. Wilson monitoring site. (Excluding mixing ratios measured on February 14, 2008 when winds were from the north. Note: the dotted line represents the average mixing ratio of each hour.)

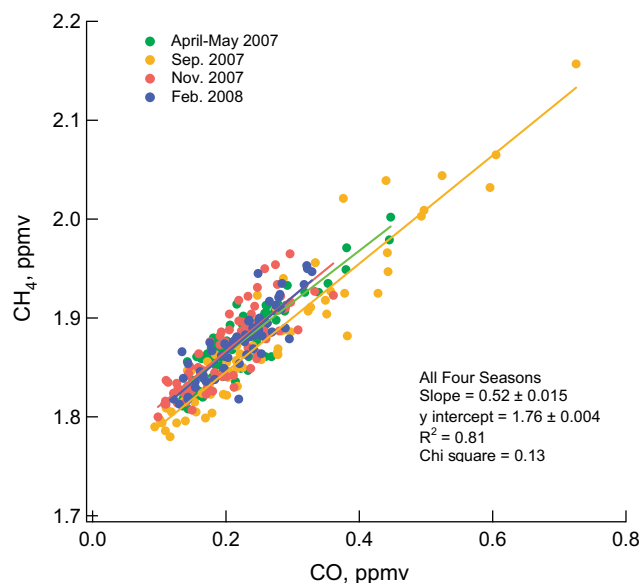


Fig. 4. Correlation of CH_4 and CO mixing ratios measured between 11 am and 6 pm at the Mt. Wilson monitoring station during four discrete seasonal campaigns (excluding north wind hours).

As a quality assurance measure, the CH_4 and CO correlation result was compared with the previous NOAA aircraft measurements collected within the mixing layer over the LA urban area during a single flight on May 13th, 2002. These aircraft measurements reveal a similar linear regression slope (0.46, Parrish, 2008) and correlation ($R^2 = 0.86$) to those collected at the MW site. Consistency between these two approaches indicates that the MW site is a representative location to evaluate the CH_4 emission inventory for LA County.

3.3. Estimate of LA County CH_4 emissions based on atmospheric mixing ratios

This section describes a “top–down” approach to calculate the total average CH_4 emission rate for LA County based on the CH_4 and CO relationship observed at MW and the CO emissions inventory. A scaling ratio (or enhancement factor) method using correlation of pollutant mixing ratios above the background to estimate trace gas emissions was utilized. This “top–down” approach relies on the fact that both CH_4 and CO are non-reactive on the time scale of

dispersion. The atmospheric lifetime of CH_4 is estimated to be 8–12 years (NOAA, 2000; Cunnold et al., 2002; IPCC, 2007). Carbon monoxide is an excellent tracer for observing global transport in the troposphere (NCAR, 1999). Its lifetime of one to three months depending upon season is long enough for the gas to be tracked as it rises from the surface and journeys around the globe. Additionally, CO emission sources are mostly associated with human activities, primarily on-road and off-road vehicles in the LA Basin. The accuracy of this “top–down” approach relies both on the quality of the CARB CO inventory, which has been developed over decades using extensive monitoring programs with validation from ambient ratio studies, tunnel studies, fuel-based inventories, and remote sensing techniques (Singer and Harley, 2000; Marr et al., 2002; Wenzel, 2005; Wunch et al., 2008), and on the validity of the assumption that the approximately constant CH_4 to CO ratio observed at MW is representative of the total emission of the LA County area.

Sources of both CH_4 and CO are likely to be similarly distributed (e.g., with population) and subject to similar scales of atmospheric transport and dilution. Also, as discussed in the previous section, both gases are well-mixed before reaching the MW site and source contributions of both compounds are reasonably consistent. Thus, the slope of the regression line for concentrations of CH_4 and CO allows scaling the local CH_4 emissions to the local CO emissions. This methodology was applied by Warneke et al. (2007) to estimate emissions of volatile organic compounds (VOCs) for comparison with the United States Environmental Protection Agency (EPA) National Emissions Inventory (NEI) database. Other research groups using this methodology include scientists conducting the Advanced Global Atmospheric Gases Experiment (AGAGE), which has been measuring compositions of the global atmosphere continuously since 1978. Greally et al. (2007) and Reimann et al. (2005) of AGAGE used the trace gas to CO scaling ratio method to estimate emissions inventories for HFC-152a and methyl chloroform. Wiedinmyer and Friedli (2007) calculated emission factors for mercury (Hg) from fires using correlation of measured Hg and CO in a fire plume based on a similar scaling ratio approach. Additionally, this atmospheric concentration ratio analysis was presented by CARB as one of the three verification methods in the 1997 Senate Bill 2174 (Health and Safety Code section 39 607.3) staff report (CARB, 1997).

The scaling ratio approach typically utilizes the linear regression slope of the two compounds under consideration as provided in Fig. 4 (Warneke et al., 2006, 2007). Using this relationship, the MW scaling ratio ($\Delta\text{CH}_4 = \text{slope} \times \Delta\text{CO}$) combined with the total CO emissions from the CARB inventory (CARB, 2005) gives the CH_4 emissions for LA County. Fig. 4 provides the CH_4 and CO mixing ratios regression trend line slope (0.52) and its uncertainty (± 0.015) from all four seasonal sampling campaigns, with the exception of the data collected on February 14, 2008 when the winds were from the north. The regression trend line intercept (i.e., 1.76) in the scatter plot (Fig. 4) is the result of both CH_4 and CO background mixing ratios measured at the MW site. The estimated CH_4 inventory is calculated using Equation (1), which includes the respective compound molecular weights to convert from volume concentration to mass units.

$$\text{CH}_4 \text{ metric tons} = (\text{CO metric tons})(0.52 \pm 0.015)(16/28) \quad (1)$$

The 2007 SoCAB portion of LA County CO emissions (1800 metric tons day^{-1}) is available from CARB’s Emission Forecasting System (CARB, 2008b). The CO inventory includes anthropogenic emissions only (i.e., not including wildfires emissions), since there were no known wildfires near the MW monitoring station during the period of study. This CO inventory is incorporated into Equation (2) which calculates annual CH_4 emissions for LA County.

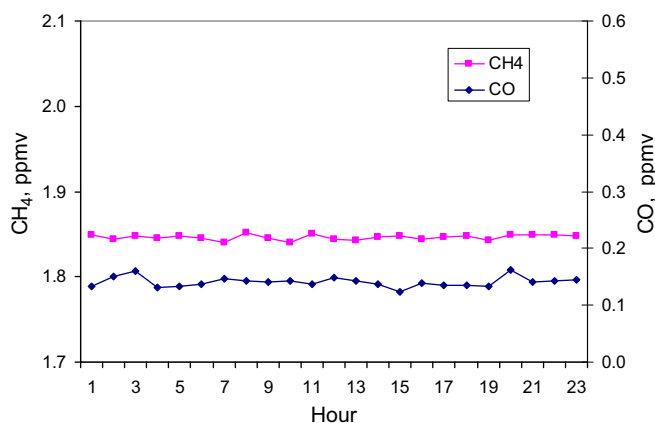


Fig. 5. Nearly constant CH_4 and CO mixing ratios measured on February 14, 2008 when north winds dominated.

CH₄ metric tons year⁻¹

$$\begin{aligned}
 &= (1800 \text{ metric tons day}^{-1}) \times (0.52 \pm 0.015) \\
 &\quad \times (16/28) \times 365 (\text{day year}^{-1}) \\
 &= 200,000 \pm 5600 \text{ metric tons of CH}_4 \text{ year}^{-1} \\
 &= 4.2 \pm 0.12 \text{ MMT CO}_2 \text{ E year}^{-1} \quad (2)
 \end{aligned}$$

The unit of MMT – million metric tons or teragrams (Tg) – CO₂ E accounts for the greater Global Warming Potential (GWP) of CH₄, which is 21 times the GWP of CO₂ (for consistency with CARB's GHG inventory methodology). Note that the estimated CH₄ emissions uncertainty reflects only the error in the slope determination from the regression between CH₄ and CO mixing ratios. Additional uncertainty due to LA County CO emissions should be considered (see Equation (2)); however, this value is currently not available.

3.4. Statewide and LA County CH₄ emissions – based on IPCC methods

In order to evaluate the accuracy of CARB's "bottom-up" CH₄ inventory, via comparison with the "top-down" inventory based on the observations at MW, it must be disaggregated to LA County for the same geographic scale. The majority (93%) of the CH₄ statewide inventory was originally calculated using data with spatial information. For example, livestock populations and locations are available from California Department of Food and Agriculture (California Department of Food and Agriculture, 2008). There are no known livestock activities in the study area, which is the SoCAB portion of LA County. Methane emissions from this sector are assumed to be zero. Locations and operation parameters of landfills and wastewater treatment plants are well-documented. Their CH₄ emissions are available for LA County (Hunsaker, 2008). Natural gas transmission losses are calculated by air districts and available in the CARB emission inventory database (CARB, 2008b). Methane emissions from these sources in LA County are compiled by CARB (Hunsaker, 2008). Allocation of CH₄ emissions from the transportation sector for LA County is based on CARB's on-road and off-road emission inventory models (Hanemann et al., 2008). Finally, there is no known rice cultivation in LA County. Using these described emission activities, Table 1 summarizes both the statewide and the SoCAB portion of LA County CH₄ emissions.

Because the CARB "bottom-up" CH₄ inventories are only available for calendar years 1990 through 2004, an assumption was made that the most recent 2004 CH₄ emissions were the same as in 2007 and 2008 (the years when CH₄ and CO mixing ratios were measured at MW). Since the projection of the CARB official "bottom-up" inventory to the 2007–2008 CH₄ emissions will involve additional uncertainty and we do not anticipate there would be significant changes in the CH₄ inventory based on the

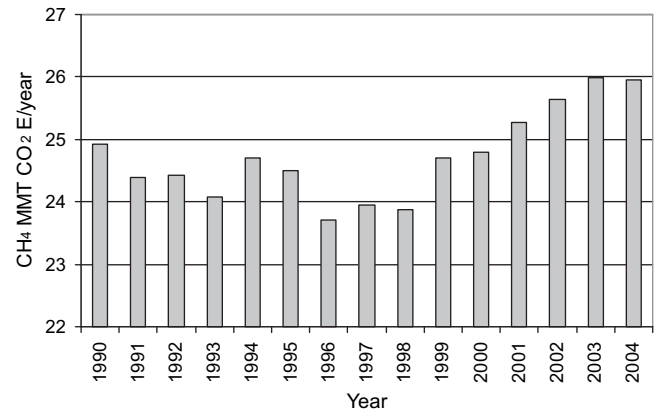


Fig. 6. Statewide CH₄ emissions inventoried for 1990–2004 (MMT CO₂ E year⁻¹, CARB, 2008a).

historical trend (Fig. 6), we assume the CARB "official" 2004 and 2007–2008 CH₄ inventories are the same, or 26 MMT CO₂ E year⁻¹ (CARB, 2008a). This statewide CH₄ inventory is allocated to the SoCAB portion of LA County (3.0 MMT CO₂ E year⁻¹, Table 1) and compared to the "top-down" estimate (4.2 ± 0.12 MMT CO₂ E year⁻¹, Equation (2)) measured at MW.

3.5. Uncertainties in inventory sectors

This section describes several uncertainties identified in the current study. First, the "top-down" inventory was estimated based on the ambient atmospheric measurements observed in 2007 and 2008, while the CARB "bottom-up" statewide CH₄ emissions were only available for up to 2004. Using the same increasing growth trend (Fig. 6), the CH₄ inventory discrepancies could be smaller than they are shown in Table 3. Secondly, there might be natural CH₄ emissions contributing to the MW site which could lead to an overestimate of CH₄ emissions, e.g., CH₄ from seeps on the ocean floor near Santa Barbara (UCSB, 2007). However, according to Mau et al. (2007), the emitted CH₄ from the Santa Barbara Channel is on the order of 0.006 MMT CO₂ E year⁻¹, which is insignificant as compared to the emissions shown in Table 1. Wetlands are another natural CH₄ emission source. According to Potter et al. (2006), biogenic CH₄ emissions from wetlands in LA County are negligible. It is therefore fair to neglect natural CH₄ emissions in LA County. Finally, an important source of uncertainty is the CO inventory, which is used as the basis (see Equations (1) and (2)) to estimate CH₄ emissions. In the literature, Marr et al. (2002) reported the fuel-based CO emissions inventory was 10–50% less than the one estimated by CARB's motor vehicle emission factor model (EMFAC). However, a recent study estimated 2004 CO emissions inventory in the SoCAB, using a remote sensing technique and EMFAC model with statewide fuel sales data, and both methods yield identical results (Wenzel, 2005).

Table 1
CARB Year 2004 statewide and SoCAB portion of LA County CH₄ inventories.

Sector	Statewide emissions ^a	SoCAB portion of LA County emissions ^a	Major sources
Agriculture & forestry	0.81	0.06	Rice cultivation ^b
Fuel combustion	1.0	0.21	Transportation
Fugitive emissions	2.6	0.01	Natural gas pipelines
Wastewater treatment	2.8	0.77	
Landfills	5.6	1.9	
Livestock	13	0	Dairy and beef cows ^b
Total	26	3.0	

Data Source – California Greenhouse Gas Emissions Inventory (CARB, 2008a).

^a MMT CO₂ E year⁻¹.

^b There is no known rice cultivation or dairy activities in LA County.

Table 2
Correlation of CH₄ and CO mixing ratios measured between 11 am and 6 pm at the Mt. Wilson monitoring station.

Season	Overall	April–May	September	November	February
Slope ± One	0.52 ± 0.015	0.52 ± 0.030	0.55 ± 0.021	0.55 ± 0.043	0.58 ± 0.043
standard deviation	1.76 ± 0.004	1.76 ± 0.007	1.74 ± 0.006	1.76 ± 0.009	1.75 ± 0.009
Intercept ± One	0.13	0.020	0.039	0.035	0.018
standard deviation	0.81	0.81	0.90	0.70	0.75
Chi Sq.					
R ²					

Table 3
Comparison of estimated LA County anthropogenic CH₄ inventories.

Methods	MMT CO ₂ E year ⁻¹	Notes
CH ₄ to CO scaling measured at Mt. Wilson	4.2 ± 0.12 ^a	Estimate
CARB CH ₄ inventory	3.0	IPCC methods

^a Note that the estimated CH₄ emissions uncertainty reflects only the error in the slope determination from the regression between CH₄ and CO mixing ratios. Additional uncertainty due to LA County CO emissions should be considered (see Equation (2)); however, this value is currently not available.

In addition, there are known uncertainties in GHG inventory methods. For example, there are concerns about the default landfill gas collection efficiency and landfill gas emissions models (CARB, 2008a). Based on the default landfill inventory method, 75% of CH₄ generated from landfills is assumed to be removed with collection systems and the remaining 25% of CH₄ generated is either oxidized (approximately 10% of the total) by microorganisms in cover soil or emitted to the atmosphere. Some landfill operators in SoCAB have questioned the appropriateness of the default 75% collection efficiency and claim to have higher collection efficiencies (Hunsaker, 2008). Methane emissions from landfills have been estimated by the First Order Decay method. This method assumes that the degradable organic component in waste decays slowly throughout a few decades, during which CH₄ and CO₂ are formed. If conditions are constant, the rate of CH₄ production depends solely on the amount of carbon remaining in the waste. As a result, emissions of CH₄ from waste deposited in a disposal site are highest in the first few years after deposition, and then gradually decline as the degradable carbon in the waste is consumed by the bacteria responsible for the decay.

Another source of possible error is the fugitive CH₄ emissions from the natural gas distribution systems. Despite the fact that the SoCAB portion of LA County has 27% of the statewide population, the CARB CH₄ inventory only attributes 0.4% of the statewide fugitive CH₄ emissions from natural gas systems to LA County (Table 1). Since natural gas consumption and distribution systems are likely associated with population, fugitive CH₄ emissions from this sector should be reviewed.

Other sources of uncertainty include emissions from interstate (e.g., aircraft and trains) and international (e.g., ocean-going ships) transport which are not well accounted for in the CARB “official” statewide GHG inventory. However, aircraft and ocean-going vessels burn jet fuel and diesel, and consequently emit very little CH₄ (EPA, 2008).

4. Conclusions and next steps

The comparison of estimated anthropogenic CH₄ inventories for the SoCAB portion of LA County is presented in Table 3. It is estimated that the “top–down” CH₄ inventory based on the mixing ratios measured at MW is approximately one-third greater than the CARB “official” statewide inventory when it is allocated to LA County. Considering the many possible uncertainties described above, the two estimates are in reasonable agreement, but this difference may still suggest under and/or uninventoried sources of CH₄ in LA County. More work is required to better quantify the CH₄ emissions from each of the large source sectors listed in Table 1, with perhaps special focus on CH₄ fugitive emissions.

Finally, the data and analysis presented here demonstrate that the MW site is a very useful location for applying the scaling factor method to develop a “top–down” CH₄ inventory for the SoCAB portion of LA County. The CH₄ and CO correlation results from the present study agree well with the NOAA WP-3 aircraft study in the mixing layer over the LA urban area in 2002. We plan to apply this

scaling factor method to other GHGs and in other air basins, in order to evaluate emissions inventories and to investigate whether there are uninventoried GHG sources in California.

Acknowledgments

The authors acknowledge the contribution and support of the following individuals: Bart Croes, Jim Pederson, Eileen McCauley, Michael Poore, Ken Stroud, Kathy Gill, Steve Rider, Mac McDougall, Arthur Marsh, and Curt Schreiber of CARB, and are grateful to Eliot Atlas of the University of Miami for providing the 2002 NOAA WP-3 aircraft data.

References

- California Air Resources Board, 1997. Public meeting to consider approval and verification of the California Emission Inventory.
- California Air Resources Board, 2005. The California Almanac of Emissions and Air Quality – 2005 Edition, <http://www.arb.ca.gov/aqd/almanac05/almanac05.htm>.
- California Air Resources Board, 2008a. California Greenhouse Gas Emissions Inventory, <http://www.arb.ca.gov/cc/inventory/inventory.htm>, (accessed 15.08.08).
- California Air Resources Board, 2008b. California Emission Forecasting System, <http://www.arb.ca.gov/app/emsinv/fcemsumcat2007.php>, (accessed 28.10.08).
- California Department of Food and Agriculture, 2008. California Dairy Statistics 2006 – Statistics & Trends, <http://www.cdffa.ca.gov/dairy/pdf/annual/2006/cadairystatistics2006.pdf>, (accessed 22.04.08).
- COLC, 2006. California Office of Legislative Counsel, California Global.
- Cunnold, D.M., Steele, L.P., Fraser, P.J., Simmonds, P.G., Prinn, R.G., Weiss, R.F., Porter, L.W., O'Doherty, S., Langenfelds, R.L., Krummel, R.B., Wang, H.J., Emmons, L., Tie, X.X., Dlugokencky, E.J., 2002. In situ measurements of atmospheric methane at GAGE/AGAGE sites during 1985–2000 and resulting source inferences. *Journal of Geophysical Research* 107 (D14), 4225. doi:10.1029/2001JD001226.
- Dlugokencky, E.J., Masarie, K.A., Lang, P.M., Tans, P.P., Steele, L.P., Nisbet, E.G., 1994. A dramatic decrease in the growth rate of atmospheric methane in the northern hemisphere during 1992. *Geophysical Research Letters* 21, 45–48.
- Dlugokencky, E.J., Dutton, E.G., Novelli, P.C., Tans, P.P., Masarie, K.A., Lantz, K.O., Madronich, S., 1996. Changes in CH₄ and CO growth rates after the eruption of Mt. Pinatubo and their link with changes in tropical tropospheric UV flux. *Geophysical Research Letters* 23, 2761–2764.
- Dlugokencky, E.J., Masarie, K.A., Lang, P.M., Tans, P.P., 1998. Continuing decline in the growth rate of the atmospheric methane burden. *Nature* 393, 447–450.
- Dlugokencky, E.J., Houweling, S., Bruhwiler, L., Masarie, K.A., Lang, P.M., Miller, J.B., Tans, P.P., 2003. Atmospheric methane levels off: temporary pause or a new steady-state? *Geophysical Research Letters* 30 (19), 1992. doi:10.1029/2003GL018126.
- Duncan, B.N., Bey, I., Chin, M., Mickley, L.J., Fairlie, T.D., Martin, R.V., Matsueda, H., 2003. Indonesian wildfires of 1997: impact on tropospheric chemistry. *Journal of Geophysical Research* 108 (D15), 4458. doi:10.1029/2002JD003195.
- EPA, 2008. U.S. Environmental Protection Agency, SPECIATE 4.0 Database, <http://www.epa.gov/ttn/chief/software/speciate/>, (accessed 1.10.08).
- Grallly, B.R., Manning, A.J., Reimann, S., McCulloch, A., Huang, J., Dunse, B.L., Simmonds, P.G., Prinn, R.G., Fraser, P.J., Cunnold, D.M., O'Doherty, S.L., Porter, W., Stemmler, K.M., Vollmer, K., Lunder, C.R., Schmidbauer, N., Hermansen, O., Arduini, J., Salameh, P.K., Krummel, P.B., Wang, R.H.J., Folini, D., Weiss, R.F., Maione, M., Nickless, G., Stordal, F., Derwent, R.G., 2007. Observations of 1,1-difluoroethane (HFC-152a) at AGAGE and SOGE monitoring stations in 1994–2004 and derived global and regional emission estimates. *Journal of Geophysical Research* 112, D06308. doi:10.1029/2006JD007527.
- Hanemann, M., Can, S., Wenzel, T., Price, L., 2008. Improving the carbon dioxide emission estimates from the combustion of fossil fuels in California and spatial disaggregated estimate of energy-related carbon dioxide for California, final report prepared for the California Air Resources Board.
- Hofmann, D.J., Butler, J.H., Dlugokencky, E.J., Elkins, J.W., Masarie, K., Montzka, S.A., Tans, P., 2006. The role of carbon dioxide in climate forcing from 1979–2004: introduction of the annual greenhouse gas index. *Tellus, Ser. B* 58, 614–619.
- Hunsaker, L., 2008. Larry Hunsaker of California Air Resources Board, Emission Inventory Branch, personal communication with Ying Hsu.
- IPCC, 2007. Climate change 2007: the physical science basis. In: Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K.B., Tignor, M., Miller, H.L. (Eds.), Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, p. 996.
- Marr, L.C., Black, D.R., Harley, R.A., 2002. Formation of photochemical air pollution in central California 1. Development of a revised motor vehicle emission inventory. *Journal of Geophysical Research* 107 (D6), 4047. doi:10.1029/2001JD000689.
- Mau, S., Valentine, D.L., Clark, J.F., Reed, J., Camilli, R., Washburn, L., 2007. Dissolved methane distributions and air–sea flux in the plume of a massive seep field,

- Coal Oil Point, California. *Journal of Geophysical Research* 34, L22603. doi:10.1029/2007GL031344.
- NCAR, 1999. New satellite-borne instrument to measure carbon monoxide pollution in the lower atmosphere, National Center for Atmospheric Research news release (December 21, 1999), <http://www.ucar.edu/communications/newsreleases/1999/mopitt99.html>.
- NOAA, 2000. National Oceanic and Atmospheric Administration. September 2000, retrieved on January 15, 2008. Newsletter (Issue 21). http://www.igac.noaa.gov/newsletter/21/methane_sink.php.
- NOAA, 2008. National Oceanic and Atmospheric Administration, Interactive Atmospheric Data Visualization, 2003–2008 airborne methane mixing ratios measured 1000–2000 meters above sea level over Trinidad Head, California, accessed on September 25th, 2008, <http://www.esrl.noaa.gov/gmd/ccgg/iadv/>.
- Parrish, D., 2008. David Parrish of National Oceanic and Atmospheric Administration personal communication with Ying Hsu on September 10, 2008, draft NOAA Science Plan, data collected during the NOAA 2002 aircraft study over Los Angeles urban area.
- Potter, C., Klooster, S., Hiatt, S., Fladeland, M., Genovese, V., Gross, P., 2006. Methane emissions from natural wetlands in the United States: satellite-derived estimation based on ecosystem carbon cycling. *Earth Interactions* 10 paper no. 22.
- Prinn, R.G., Weiss, R.F., Miller, B.R., Huang, J., Alyea, F.N., Cunnold, D.M., Fraser, P.J., Hartley, D.E., Simmonds, P.G., 1995. Atmospheric trends and lifetime of CH_2Cl_2 and global OH concentrations. *Science* 269, 187–192.
- Prinn, R.G., Huang, J., Weiss, R.F., Cunnold, D.M., Fraser, P.J., Simmonds, P.G., McCulloch, A., Harth, C., Salameh, P., O'Doherty, S., Wang, R.H.J., Porter, L., Miller, B.R., 2001. Evidence for substantial variations of atmospheric hydroxyl radicals in the last two decades. *Science* 292, 1882–1888.
- Prinn, R.G., Huang, J., Weiss, R.F., Cunnold, D.M., Fraser, P.J., Simmonds, P.G., McCulloch, A., Harth, C., Reimann, S., Salameh, P., O'Doherty, S., Wang, R.H.J., Porter, L., Miller, B.R., Krummel, P.B., 2005. Evidence for variability of atmospheric hydroxyl radicals over the past quarter century. *Geophysical Research Letters* 32, L07809. doi:10.1029/2004GL022228.
- Reimann, S., Manning, A.J., Simmonds, P.G., Cunnold, D.M., Wang, R.H.J., Li, J., McCulloch, A., Prinn, R.G., Huang, J., Weiss, R.F., Fraser, P.J., O'Doherty, S., Grealley, B.R., Stemmler, K., Hill, M., Folini, D., 2005. Low European methyl chloroform emissions inferred from long-term atmospheric measurements. *Nature* 433, 506–509.
- Simpson, I.J., Blake, D.R., Rowland, F.S., Chen, T.Y., 2002. Implications of the recent fluctuations in the growth rate of tropospheric methane. *Geophysical Research Letters* 29 (10), 1479. doi:10.1029/2001GL014521.
- Simpson, I.J., Rowland, F.S., Meinardi, S., Balke, D.R., 2006. Influence of biomass burning during recent fluctuations in the slow growth of global tropospheric methane. *Geophysical Research Letters* 33, L22808. doi:10.1029/2006GL027330.
- Singer, B., Harley, R.A., 2000. A fuel-based inventory of motor vehicle exhaust emissions in the Los Angeles area during summer 1997. *Atmospheric Environment* 34, 1783–1795.
- Stolzenbach, K.D., Lu, R., Xiong, C., Friedlander, S., Turco, R., Schiff, K., Tiefenthaler, L., 2001. Measuring and modeling of atmospheric deposition on Santa Monica Bay and the Santa Monica Bay Watershed. Report to the Santa Monica Bay Restoration Project.
- UCSB, 2007. University of California at Santa Barbara, press release on December 20, 2007, Scientists find good news about methane bubbling up from the ocean floor near Santa Barbara, <http://www.ia.ucsb.edu/pa/display.aspx?pkey=1704>.
- VanCuren, R.A., 2008. Inferring High-GWP Emissions from the Los Angeles Urban Area by Association with Common Air Pollutant Species, *Eos Trans. AGU*, 89(53), Fall Meet. Suppl., Abstract A53H-02.
- Warming Solutions Act of 2006, Assembly Bill No. 32, http://www.leginfo.ca.gov/pub/05-06/bill/asm/ab_0001-0050/ab_32_bill_20060927_chaptered.pdf.
- Warneke, C., de Gouw, J.A., Stohl, A., Cooper, O.R., Goldan, P.D., Kuster, W.C., Holloway, J.S., Williams, E.J., Lerner, B.M., McKeen, S.A., Trainer, M., Fehsenfeld, F.C., Atlas, E.L., Donnelly, S.G., Stroud, V., Lueb, A., Kato, S., 2006. Biomass burning and anthropogenic sources of CO over New England in the summer 2004. *Journal of Geophysical Research* 111, D23S15. doi:10.1029/2005JD006878.
- Warneke, C., McKeen, S.A., de Gouw, J.A., Goldan, P.D., Kuster, W.C., Holloway, J.S., Williams, E.J., Lerner, B.M., Parrish, D.D., Trainer, M., Fehsenfeld, F.C., Kato, S., Atlas, E.L., Baker, A., Blake, D.R., 2007. Determination of urban volatile organic compound emission ratios and comparison with an emissions database. *Journal of Geophysical Research* 112, D10S47. doi:10.1029/2006JD007930.
- Wenzel, T., 2005. Use of California remote sensing pilot project data for on-road fleet and emissions characterization, and evaluation of the Enhanced Smog Check program, final report to California Bureau of Automotive Repair and Air Resources Board.
- Wiedinmyer, C., Friedli, H., 2007. Mercury emission estimates from fires: an initial inventory for the United States. *Environment Science & Technology* 41 (23), 8092–8098. doi:10.1021/ES0712890.
- Wunch, D., Wennberg, P.O., Toon, G.C., Keppel-Aleks, G., Yavin, Y.G., 2008. Methane, nitrous oxide, carbon dioxide and carbon monoxide emissions in the South Coast air basin from September 2007 through June 2008, presented at the 2008 American Geophysical Union (AGU) meeting, <http://www.agu.org/meetings/fm08/>.